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(71) Applicant *(for all designated States except US)*: CRYOVAC, INC. [US/US]; P.O. Box 464, Duncan, SC 29334-0464 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: HERNANDEZ, Mario Alberto [MX/US]; 4821 Whisper Wind Drive, Wichita Falls, TX 76310 (US). JENSON, Kird, Edward [US/US]; 1605 Quail Valley Road, Iowa Park, TX 76367 (US). SHAH, Gautam, P. [US/US]; 27 English Oak Road, Simpsonville, SC 29681 (US). VADHAR, Parimal, M. [US/US]; 1118 N. Cedwarbluff Court, Greer, SC 29650 (US).

(74) Agents: HURLEY, Rupert, B., Jr. et al.; 100 Rogers Bridge Road, P.O. Box 464, Duncan, SC 29334 (US).

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(54) Title: MULTILAYER PACKAGING FILM CONTAINING CARBON BLACK

(57) Abstract

An opaque multilayer film which is especially suited to packaging light sensitive products such as photographic film and photographic paper has an outer seal layer and at least one inner layer containing carbon black, as well as a layer which serves as a moisture barrier layer. The presence of the carbon black in an inner film layer prevents the carbon black from rubbing off of the film on film-making and packaging equipment, as well as a product packaged in the film. Preferably the film has high abuse-resistance, high puncture-resistance, and good sealability. Articles such as bags, casings, and pouches can be made from the film.

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MULTILAYER PACKAGING FILM CONTAINING CARBON BLACK

Background of the Invention

Light-sensitive products, such as photographic film and photographic paper, are often packaged in opaque packages in order to keep light from adversely affecting the product. A superior package for such products would also provide high abuse-resistance, high moisture barrier, and high O_2-barrier.

Summary of the Invention

The present invention relates to films, and articles made therefrom, which are designed for packaging light-sensitive products, especially motion picture film rolls and rolls of photographic paper. The film according to the present invention preferably has high opacity, as well as high abuse-resistance and high puncture-resistance. Optionally, the film can be of a type which, when heat sealed to itself or another film, exhibits a high burst strength. In addition, the film can be made from relatively inexpensive polymers, and need not require complex production processes, such as cross-lamination.

As a first aspect, the present invention pertains to a multilayer film comprising four layers. The first layer comprises at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester; the second layer comprises carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester; the third layer comprises at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester; and, the fourth layer comprises at least one member selected from the group consisting of high density polyethylene, propylene homopolymer, polyvinylidene chloride, fluoropolymer, and aluminum. The second layer is between the first layer and the third layer, and the third layer is between the second layer and the fourth layer.

Preferably the fourth layer has a moisture vapor transmission rate of less than about 0.3 grams/100sq.in. at 100°F and 90% relative humidity; more preferably, less than about 0.2 grams/100sq.in. at 100°F and 90% relative humidity; still more preferably, less than about 0.15 grams/100sq.in. at 100°F and 90% relative humidity.

Preferably, the multilayer film has a thickness of from about 2 to 10 mils; more preferably, from about 3 to 8 mils; still more preferably, from about 4 to 7 mils; and, yet still more preferably, about 5 mils. Preferably, at least a portion of the film has been irradiated to a level of from about 50 to 150 kilograys. Preferably, the film has a total free shrink of from about 0 to 30 percent; more preferably, from about 0 to 20 percent; still more preferably, from about 0 to 10 percent; and, yet still more preferably, from about 0 to 7 percent.

In a first preferred film having additional layers, the fourth layer comprises high density polyethylene, with the fifth layer preferably comprising at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, polyvinylidene chloride, polyamide, polyester, aluminum, and polyacrylonitrile, the fifth layer being between the third layer and the fourth layer; and the sixth layer preferably comprising biaxially oriented polypropylene, with the sixth layer being between the third layer and the fourth layer.

In the second preferred film having additional layers, a fifth layer comprises at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester, the fifth layer being between the third layer and the fourth layer; a sixth layer comprises carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester, the sixth layer being between the third layer and the fifth layer; and, a seventh layer comprises at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester, the seventh layer being between the third layer and the sixth layer. Preferably, the first, second, third, fifth, sixth, and seventh layers comprise a structure which is symmetrical in both thickness and chemical composition.

Preferably, the multilayer film further comprises an eighth layer comprising: (a) from about 1 to 40 weight percent of a first polymer comprising at least one member selected from the group consisting of ionomer and ethylene/vinyl acetate copolymer, wherein the first polymer has a melt flow index of less than 5; and (b) from about 60 to 99 weight percent of a second polymer comprising at least one member selected from the group consisting of low density polyethylene, ethylene/vinyl acetate copolymer, and modified ethylene/vinyl acetate copolymer, the second polymer having a melt index greater than 20, wherein the second polymer comprises low density polyethylene if the first polymer comprises ethylene/vinyl acetate copolymer. A copolyester is a preferred polyester for one or more of the at least one member selected from the group consisting of the first layer, the second layer, the third layer, the fifth layer, the sixth layer, and the seventh layer. Preferably, the first, second, fifth, and sixth layers each comprise a blend of ethylene/vinyl acetate copolymer and linear low density polyethylene; the third and seventh layers each comprise ethylene/vinyl acetate copolymer; and the fourth layer comprises high density polyethylene. Preferably, the film first, second, third, fifth, sixth, and seventh layers each comprise biaxially oriented polymer. Preferably, at least the first, second, third, fifth, sixth, and seventh layers comprise a crosslinked polymer network. Preferably, the multilayer film has an O_2-transmission rate of less than about 100 cc/m^2 day stp at 100% relative humidity; more preferably, less than 50 cc/m^2 day stp at 100% relative humidity; still more preferably, less than 20 cc/m^2 day stp at 100% relative humidity.

In a first species of this second preferred film having additional layers, preferably the fourth layer comprises high density polyethylene, with the multilayer film further comprising: (a) an eighth layer comprising at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, polyvinylidene chloride, amorphous polyamide, polyester, and polyacrylonitrile, the eighth layer being between the fifth layer and the fourth layer (more preferably, BAREX® acrylonitirle methylacrylate copolymer); and (b) a ninth layer comprising biaxially oriented polypropylene, the ninth layer being between the fifth layer and the fourth layer.

In a second species of this second preferred film having additional layers, preferably the fourth layer comprises high density polyethylene, with the multilayer film further comprising: (a) an eighth layer comprising high density polyethylene, the eighth layer being between the fifth layer and the fourth layer; and, (b) a ninth layer comprising at least one

member selected from the group consisting of ethylene/vinyl alcohol copolymer, polyvinylidene chloride, amorphous polyamide, polyester, and polyacrylonitrile, the eighth layer being between the fifth layer and the fourth layer. A preferred polyacrylonitrile is BAREX acrylonitirle methylacrylate copolymer, supplied by the BP Chemical Co. Preferably, the ninth layer comprises biaxially-oriented polypropylene. Preferably, the ninth layer comprises propylene homopolymer in an amount of from about 60 to 99 weight percent, based on layer weight, and hydrocarbon resin in an amount of from about 1 to 40 weight percent, based on layer weight; more preferably, from about 15 to 20 weight percent. Preferably, the copolyester is present in at least one member selected from the group consisting of the first layer, the second layer, the third layer, the fifth layer, the sixth layer, the seventh layer, and the eighth layer. Preferably, the first, second, fifth, and sixth layers each comprise a blend of ethylene/vinyl acetate copolymer and linear low density polyethylene; the third and seventh layers each comprise ethylene/vinyl acetate copolymer; the fourth layer comprises high density polyethylene; the eighth layer comprises polyvinylidene chloride; and the ninth layer comprises biaxially oriented polypropylene.

As a second aspect, the present invention is directed to an easy-open article having a peel opening force of less than about 2.5 pounds per inch. The article comprises a first film sealed to itself or a second film. The first film comprises: (A) an first layer which is an outer film layer and which serves as a seal layer, the first layer comprising: (i) from about 1 to 40 weight percent of a first polymer comprising at least one member selected from the group consisting of ionomer and ethylene/vinyl acetate copolymer, wherein the first polymer has a melt flow index of less than 5; and (ii) from about 60 to 99 weight percent of a second polymer comprising at least one member selected from the group consisting of low density polyethylene, ethylene/vinyl acetate copolymer, and modified ethylene/vinyl acetate copolymer, the second polymer having a melt index greater than 20, wherein the second polymer comprises low density polyethylene if the first polymer comprises ethylene/vinyl acetate copolymer. The second layer comprises at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester. The third layer comprises carbon black pigment and at least one member selected from the group consisting of linear low

density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester. The fourth layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester. The fifth layer comprising at least one member selected from the group consisting of high density polyethylene, propylene homopolymer, polyvinylidene chloride, fluoropolymer, and aluminum. The third layer is between the second layer and the fourth layer, and the fourth layer is between the third layer and the fifth layer.

As a third aspect, the present invention is directed to an article comprising a multilayer film sealed to itself or another film, wherein the multilayer film comprises: (A) a first layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester; (B) a second layer comprising carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester; (C) a third layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester; and (D) a fourth layer comprising at least one member selected from the group consisting of high density polyethylene, propylene homopolymer, polyvinylidene chloride, fluoropolymer, and aluminum. The second layer is between the first layer and the third layer, and the third layer is between the second layer and the fourth layer. Preferably, the article is an end-seal bag, side-seal bag, L-seal bag, pouch, and backseamed casing. Preferably, the article has a burst strength of at least about 200 inches of water; more preferably, from about 200 to 500 inches of water; still more preferably, from about 220 to 400 inches of water; yet still more preferably, from about 230

to 350 inches of water; and, even yet still more preferably, from about 240 to 280 inches of water.

Brief Description of the Drawings

Figure 1 illustrates a schematic view of a preferred end-seal bag according to the present invention, in a lay-flat view.

Figure 2 illustrates a schematic view of a preferred side-seal bag according to the present invention, in a lay-flat view.

Figure 3 illustrates a schematic view of a preferred pouch according to the present invention, in a lay-flat view.

Figure 4 illustrates a cross-sectional view of a preferred multilayer film suitable for use in the articles illustrated in Figures 1-3.

Figure 5 illustrates a schematic view of a preferred process for making the multilayer films illustrated in Figures 4.

Detailed Description of the Invention

As used herein, the phrase "lay-flat film" refers to a film that has been extruded as a wide, thin-walled, circular tube, usually blown, cooled, then gathered by converging sets of rollers and wound up in flattened form. The phrase "lay-flat width", refers to half of the circumference of the inflated film tube.

Films of and used in the present invention have a thickness of 0.25 mm or less, i.e., 10 mils or less. As used herein, the term "package" refers to packaging materials configured around a product being packaged. The phrase "packaged product," as used herein, refers to the combination of a product which is surrounded by a packaging material.

As used herein, the term "seal" refers to any seal of a first region of a film surface to a second region of a film surface, wherein the seal is formed by heating the regions to at least their respective seal initiation temperatures, i.e., a heat seal. The sealing can be performed by any one or more of a wide variety of manners, such as using a heated bar, hot air, hot wire, infrared radiation, ultrasonic sealing, radio frequency sealing, etc.

Heat sealing is the process of joining two or more thermoplastic films or sheets by heating areas in contact with each other to the temperature at which fusion occurs, usually aided by pressure. When the heat is applied by dies or rotating wheels maintained at a constant temperature, the process is called thermal sealing. In melt-bead sealing, a narrow strand of molten polymer is extruded along one surface, trailed by a wheel that presses the

two surfaces together. In impulse sealing, heat is applied by resistance elements that are applied to the work when relatively cool, then are rapidly heated. Simultaneous sealing and cutting can be performed in this way. Dielectric sealing is accomplished with polar materials by inducing heat within the films by means of radio-frequency waves. When heating is performed with ultrasonic vibrations, the process is called ultrasonic sealing.

As used herein, the phrase "the layer...comprising" refers to a film layer which has the recited components throughout the entire cross-section of the layer, as opposed to having one or more of the components on the surface of the layer.

As used herein, the phrases "food-contact layer" and "meat-contact layer" refer to a layer of a multilayer film which is in direct contact with the food/meat in the package comprising the film. In a multilayer film, a food-contact layer is always an outer film layer, as the food-contact layer is in direct contact with the food product within the package. The food-contact layer is an inside layer in the sense that with respect to the packaged food product, the food-contact layer is the inside layer (i.e., innermost layer) of the package, this inside layer being in direct contact with the food. As used herein, the phrases "food-contact surface" and "meat-contact surface" refer to an outer surface of a food contact layer, this outer surface being in direct contact with the food within the package.

As used herein, "EVOH" refers to ethylene vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene vinyl acetate copolymers, and refers to a vinyl alcohol copolymer having an ethylene comonomer, and prepared by, for example, hydrolysis of vinyl acetate copolymers, or by chemical reactions with polyvinyl alcohol. The degree of hydrolysis is preferably from about 50 to 100 mole percent; more preferably, from about 85 to 100 mole percent.

As used herein, the term "barrier", and the phrase "barrier layer", as applied to films and/or film layers, are used with reference to the ability of a film or film layer to serve as a barrier to one or more gases. In the packaging art, oxygen (i.e., gaseous O_2) barrier layers have included, for example, hydrolyzed ethylene/vinyl acetate copolymer (designated by the abbreviations "EVOH" and "HEVA", and also referred to as “ethylene/vinyl alcohol copolymer”), polyvinylidene chloride, polyamide, polyester, polyacrylonitrile, etc., as known to those of skill in the art.

Copolyester is a preferred polyester for use in the present invention. As used herein, the word "copolyester" refers to a polyester with two different polyester groups in the repeating units. (See R.B. Seymour, Engineering Polymer Sourcebook (1990 McGraw Hill Publishing Company). A preferred copolyester is known as PETG copolyester 6763, marketed by Eastman Chemical Company. Others include NPG (neopentene glycol), and IMPET EKX-105 copolyester marketed by Hoechst Celaneese.

As used herein, the phrase "abuse layer", as well as the phrase "puncture-resistant layer", refer to an outer film layer and/or an inner film layer, so long as the film layer serves to resist abrasion, puncture, and other potential causes of reduction of package integrity, as well as potential causes of reduction of package appearance quality.

As used herein, the terms "lamination," "laminate," as well as the phrase "laminated film," refer to the process, and resulting product, made by bonding together two or more layers of film or other materials. Lamination can be accomplished by joining layers with adhesives, joining with heat and pressure, with corona treatment, and even spread coating and extrusion coating. The term laminate is also inclusive of coextruded multilayer films comprising one or more tie layers.

As used herein, the term "oriented" refers to a polymer-containing material which has been elongated (generally at an elevated temperature called the orientation temperature), followed by being "set" in the elongated configuration by cooling the material while substantially retaining the elongated dimensions. This combination of elongation at elevated temperature followed by cooling causes an alignment of the polymer chains to a more parallel configuration, thereby improving the mechanical properties of the film. Upon subsequently heating unrestrained, unannealed, oriented polymer-containing material to its orientation temperature, heat shrinkage is produced almost to the original dimensions, i.e., pre-elongation dimensions. The term "oriented," is herein used with reference to oriented films, which can undergo orientation in any one or more of a variety of manners.

Orienting in one direction is referred to herein as "uniaxial orientation," while orienting in two directions is referred to herein as "biaxial orientation." In oriented plastic films, there can be internal stress remaining in the plastic sheet which can be relieved by reheating the film to a temperature above that at which it was oriented. Upon reheating such a film, the film tends to shrink back to the original dimensions it

had before it was oriented. Films which shrink upon being heated are generally referred to as heat-shrinkable films.

As used herein, the phrase "orientation ratio" refers to the multiplication product of the extent to which the plastic film material is oriented in several directions, usually two directions perpendicular to one another. Orientation in the machine direction is herein referred to as "drawing", whereas orientation in the transverse direction is herein referred to as "stretching". For films extruded through an annular die, stretching is obtained by "blowing" the film to produce a bubble. For such films, drawing is obtained by passing the film through two sets of powered nip rolls, with the downstream set having a higher surface speed than the upstream set, with the resulting draw ratio being the surface speed of the downstream set of nip rolls divided by the surface speed of the upstream set of nip rolls. The degree of orientation is also referred to as the orientation ratio, also known as the "racking ratio".

Preferably, the multilayer film of the present invention has low free shrink, e.g., a total (i.e., longitudinal plus transverse) free shrink at 185°F of less than 30 percent, more preferably less than 20 percent, still more preferably, less than 10 percent, and, yet still more preferably, less than about 7 percent. This can be achieved through annealing of a film produced by a relatively low temperature orientation, or by producing a hot blown film.

As used herein, the term "monomer" refers to a relatively simple compound, usually containing carbon and of low molecular weight, which can react to form a polymer by combining with itself or with other similar molecules or compounds.

As used herein, the term "comonomer" refers to a monomer which is copolymerized with at least one different monomer in a copolymerization reaction, the result of which is a copolymer.

As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homopolymers, copolymers, terpolymers, tetrapolymers, etc. In general, the layers of a film can consist essentially of a single polymer, or can have additional polymers together therewith, i.e., blended therewith.

As used herein, the term "homopolymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single type of repeating unit.

As used herein, the term "copolymer" refers to polymers formed by the polymerization reaction of at least two different monomers. For example, the term "copolymer" includes the copolymerization reaction product of ethylene and an alpha-olefin, such as 1-hexene. The term "copolymer" is also inclusive of, for example, the copolymerization of a mixture of ethylene, propylene, 1-hexene, and 1-octene. As used herein, the term "copolymerization" refers to the simultaneous polymerization of two or more monomers. The term "copolymer" is also inclusive of random copolymers, block copolymers, and graft copolymers.

As used herein, the term "polymerization" is inclusive of homopolymerizations, copolymerizations, terpolymerizations, etc., and includes all types of copolymerizations such as random, graft, block, etc. In general, the polymers, in the films used in accordance with the present invention, can be prepared in accordance with any suitable polymerization process, including slurry polymerization, gas phase polymerization, and high pressure polymerization processes.

As used herein, a copolymer identified in terms of a plurality of monomers, e.g., "propylene/ethylene copolymer", refers to a copolymer in which either monomer may copolymerize in a higher weight or molar percent than the other monomer or monomers. However, the first listed monomer preferably polymerizes in a higher weight percent than the second listed monomer, and, for copolymers which are terpolymers, quadripolymers, etc., preferably the first monomer copolymerizes in a higher weight percent than the second monomer, and the second monomer copolymerizes in a higher weight percent than the third monomer, etc.

As used herein, terminology employing a "/" with respect to the chemical identity of a copolymer (e.g., "an ethylene/alpha-olefin copolymer"), identifies the comonomers which are copolymerized to produce the copolymer. As used herein, "ethylene alpha-olefin copolymer" is the equivalent of "ethylene/alpha-olefin copolymer."

As used herein, copolymers are identified, i.e, named, in terms of the monomers from which the copolymers are produced. For example, the phrase "propylene/ethylene copolymer" refers to a copolymer produced by the copolymerization of both propylene and ethylene, with or without additional comonomer(s). As used herein, the phrase "mer" refers to a unit of a polymer, as derived from a monomer used in the polymerization reaction. For

example, the phrase "alpha-olefin mer" refers to a unit in, for example, an ethylene/alpha-olefin copolymer, the polymerization unit being that "residue" which is derived from the alpha-olefin monomer after it reacts to become a portion of the polymer chain, i.e., that portion of the polymer contributed by an individual alpha-olefin monomer after it reacts to become a portion of the polymer chain.

As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., polymers made, for example, using conventional Ziegler-Natta catalysts. Heterogeneous polymers are useful in various layers of the film used in the present invention. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

As used herein, the phrase "heterogeneous catalyst" refers to a catalyst suitable for use in the polymerization of heterogeneous polymers, as defined above. Heterogeneous catalysts are comprised of several kinds of active sites which differ in Lewis acidity and steric environment. Ziegler-Natta catalysts are heterogeneous catalysts. Examples of Ziegler-Natta heterogeneous systems include metal halides activated by an organometallic co-catalyst, such as titanium chloride, optionally containing magnesium chloride, complexed to trialkyl aluminum and may be found in patents such as U.S. Patent No. 4,302,565, to GOEKE, et. al., and U.S. Patent No. 4,302,566, to KAROL, et. al., both of which are hereby incorporated, in their entireties, by reference thereto.

As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers can be used in various layers of multilayer films useful in the present invention. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers are typically prepared using metallocene, or other single-site type catalysis, rather than using Ziegler Natta catalysts.

More particularly, homogeneous ethylene/alpha-olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular

weight distribution (M_w/M_n), composition distribution breadth index (CDBI), narrow melting point range, and single melt point behavior. The molecular weight distribution (M_w/M_n), also known as "polydispersity," may be determined by gel permeation chromatography. Homogeneous ethylene/alpha-olefin copolymers which can be used in the present invention preferably have an M_w/M_n of less than 2.7; more preferably from about 1.9 to 2.5; still more preferably, from about 1.9 to 2.3. The composition distribution breadth index (CDBI) of such homogeneous ethylene/alpha-olefin copolymers will generally be greater than about 70 percent. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent (i.e., plus or minus 50%) of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%. The Composition Distribution Breadth Index (CDBI) is determined via the technique of Temperature Rising Elution Fractionation (TREF). CDBI determination clearly distinguishes homogeneous copolymers (i.e., narrow composition distribution as assessed by CDBI values generally above 70%) from VLDPEs available commercially which generally have a broad composition distribution as assessed by CDBI values generally less than 55%. TREF data and calculations therefrom for determination of CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, in Wild et. al., J. Poly. Sci. Poly. Phys. Ed., Vol. 20, p.441 (1982). Preferably, the homogeneous ethylene/alpha-olefin copolymers have a CDBI greater than about 70%, i.e., a CDBI of from about 70% to 99%. In general, the homogeneous ethylene/alpha-olefin copolymers useful in the present invention also exhibit a relatively narrow melting point range, in comparison with "heterogeneous copolymers", i.e., polymers having a CDBI of less than 55%. Preferably, the homogeneous ethylene/alpha-olefin copolymers exhibit an essentially singular melting point characteristic, with a peak melting point (T_m), as determined by Differential Scanning Colorimetry (DSC), of from about 60°C to 105°C. Preferably the homogeneous copolymer has a DSC peak T_m of from about 80°C to 100°C. As used herein, the phrase "essentially single melting point" means that at least about 80%, by weight, of the material corresponds to a single T_m peak at a temperature within the range of from about 60°C to 105°C, and essentially no substantial fraction of the material has a peak melting point in excess of about 115°C., as determined by DSC analysis. DSC measurements are made on

a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data, i.e., the sample is heated at a programmed rate of 10°C./min. to a temperature below its critical range. The sample is then reheated (2nd melting) at a programmed rate of 10°C/min.

A homogeneous ethylene/alpha-olefin copolymer can, in general, be prepared by the copolymerization of ethylene and any one or more alpha-olefin. Preferably, the alpha-olefin is a C_3-C_{20} alpha-monoolefin, more preferably, a C_4-C_{12} alpha-monoolefin, still more preferably, a C_4-C_8 alpha-monoolefin. Still more preferably, the alpha-olefin comprises at least one member selected from the group consisting of butene-1, hexene-1, and octene-1, i.e., 1-butene, 1-hexene, and 1-octene, respectively. Most preferably, the alpha-olefin comprises octene-1, and/or a blend of hexene-1 and butene-1.

Processes for preparing and using homogeneous polymers are disclosed in U.S. Patent No. 5,206,075, to HODGSON, Jr., U.S. Patent No. 5,241,031, to MEHTA, and PCT International Application WO 93/03093, each of which is hereby incorporated by reference thereto, in its entirety. Further details regarding the production and use of homogeneous ethylene/alpha-olefin copolymers are disclosed in PCT International Publication Number WO 90/03414, and PCT International Publication Number WO 93/03093, both of which designate Exxon Chemical Patents, Inc. as the Applicant, and both of which are hereby incorporated by reference thereto, in their respective entireties.

Still another species of homogeneous ethylene/alpha-olefin copolymers is disclosed in U.S. Patent No. 5,272,236, to LAI, et. al., and U.S. Patent No. 5,278,272, to LAI, et. al., both of which are hereby incorporated by reference thereto, in their respective entireties.

As used herein, the term "polyolefin" refers to any polymerized olefin, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted. More specifically, included in the term polyolefin are homopolymers of olefin, copolymers of olefin, copolymers of an olefin and an non-olefinic comonomer copolymerizable with the olefin, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include polyethylene homopolymer, polypropylene homopolymer, polybutene, propylene/butene copolymer, ethylene/alpha-olefin copolymer, propylene/alpha-olefin copolymer, butene/alpha-olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, ethylene/butyl acrylate copolymer, ethylene/methyl acrylate copolymer, ethylene/acrylic acid

copolymer, ethylene/methacrylic acid copolymer, modified polyolefin resin, ionomer resin, polymethylpentene, etc. Modified polyolefin resin is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. It could also be obtained by incorporating into the olefin homopolymer or copolymer, an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like.

As used herein, terms identifying polymers, such as "polyamide", "polyester", "polyurethane", etc. are inclusive of not only polymers comprising repeating units derived from monomers known to polymerize to form a polymer of the named type, but are also inclusive of comonomers, derivatives, etc. which can copolymerize with monomers known to polymerize to produce the named polymer. For example, the term "polyamide" encompasses both polymers comprising repeating units derived from monomers, such as caprolactam, which polymerize to form a polyamide, as well as copolymers derived from the copolymerization of caprolactam with a comonomer which when polymerized alone does not result in the formation of a polyamide. Furthermore, terms identifying polymers are also inclusive of "blends" of such polymers with other polymers of a different type.

As used herein, the phrases "ethylene alpha-olefin copolymer", and "ethylene/alpha-olefin copolymer", refer to such heterogeneous materials as low density polyethylene (LDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), and very low and ultra low density polyethylene (VLDPE and ULDPE); as well as to such homogeneous ethylene/alpha olefin copolymers as: metallocene-catalyzed EXACT (TM) linear homogeneous ethylene/alpha olefin copolymer resins obtainable from the Exxon Chemical Company, of Baytown, Texas, homogeneous substantially linear ethylene/alpha-olefin copolymers having long chain branching (e.g., copolymers known as AFFINITY (TM) resins, and ENGAGE (TM) resins, available from the Dow Chemical Company, of Midland, Michigan), as well as TAFMER (TM) linear homogeneous ethylene/alpha-olefin copolymer resins obtainable from the Mitsui Petrochemical Corporation. Both the heterogeneous polymers and homogeneous polymers referred to above generally include copolymers of ethylene with one or more comonomers selected from C_4 to C_{10} alpha-olefin such as butene-1 (i.e., 1-butene), hexene-1, octene-1, etc. While LDPE and MDPE are more highly

branched than LLDPE, VLDPE, ULDPE, EXACT (TM) resin, and TAFMER (TM) resin, this latter group of resins has a relatively large number of short branches rather than the longer branches present in LDPE and MDPE. AFFINITY (TM) resins and ENGAGE (TM) resins have a relatively large number of short branches in combination with a relatively small number of long-chain branches. LLDPE has a density usually in the range of from about 0.91 grams per cubic centimeter to about 0.94 grams per cubic centimeter.

In general, the ethylene/alpha-olefin copolymer comprises a copolymer resulting from the copolymerization of from about 80 to 99 weight percent ethylene and from 1 to 20 weight percent alpha-olefin. Preferably, the ethylene alpha-olefin copolymer comprises a copolymer resulting from the copolymerization of from about 85 to 95 weight percent ethylene and from 5 to 15 weight percent alpha-olefin.

As used herein, the phrases "inner layer" and "internal layer" refer to any layer, of a multilayer film, having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "inside layer" refers to an outer film layer, of a multilayer film packaging a product, which is closest to the product, relative to the other layers of the multilayer film. "Inside layer" also is used with reference to the innermost layer of a plurality of concentrically arranged layers simultaneously coextruded through an annular die.

As used herein, the phrase "outer layer" refers to any film layer of film having less than two of its principal surfaces directly adhered to another layer of the film. The phrase is inclusive of monolayer and multilayer films. All multilayer films have two, and only two, outer layers, each of which has a principal surface adhered to only one other layer of the multilayer film. In monolayer films, there is only one layer, which, of course, is an outer layer in that neither of its two principal surfaces are adhered to another layer of the film.

As used herein, the phrase "outside layer" refers to the outer layer, of a multilayer film packaging a product, which is furthest from the product relative to the other layers of the multilayer film. "Outside layer" also is used with reference to the outermost layer of a plurality of concentrically arranged layers simultaneously coextruded through an annular die.

As used herein, the phrase "directly adhered", as applied to film layers, is defined as adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other layer therebetween. In contrast, as used herein, the word "between", as applied to a

film layer expressed as being between two other specified layers, includes both direct adherence of the subject layer between to the two other layers it is between, as well as including a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

As used herein, the term "core", and the phrase "core layer", as applied to multilayer films, refer to any inner film layer which has a primary function other than serving as an adhesive or compatibilizer for adhering two layers to one another. Usually, the core layer or layers provide the multilayer film with a desired level of strength, i.e., modulus, and/or optics, and/or added abuse resistance, and/or specific impermeability.

As used herein, the phrases "seal layer," "sealing layer," "heat seal layer," and "sealant layer," refer to an outer film layer, or layers, involved in the sealing of the film to itself, another film layer of the same or another film, and/or another article which is not a film. It should also be recognized that in general, up to the outer 3 mils of a film can be involved in the sealing of the film to itself or another layer. With respect to packages having only fin-type seals, as opposed to lap-type seals, the phrase "sealant layer" generally refers to the inside film layer of a package, as well as supporting layers within 3 mils of the inside surface of the sealant layer, the inside layer frequently also serving as a food contact layer in the packaging of foods. In general, sealant layers employed in the packaging art have included thermoplastic polymers, such as polyolefin, polyamide, polyester, and polyvinyl chloride.

As used herein, the phrase "tie layer" refers to any inner film layer having the primary purpose of adhering two layers to one another. Tie layers can comprise any polymer having a polar group thereon, or any other polymer which provides sufficient interlayer adhesion to adjacent layers comprising otherwise nonadhering polymers.

As used herein, the phrase "skin layer" refers to an outside layer of a multilayer film in packaging a product, this skin layer being subject to abuse.

As used herein, the phrase "bulk layer" refers to any layer of a film which is present for the purpose of increasing the abuse-resistance, toughness, modulus, etc., of a multilayer film. Bulk layers generally comprise polymers which are inexpensive relative to other polymers in the film which provide some specific purpose unrelated to abuse-resistance, modulus, etc.

The names "first layer", "second layer", as used herein, are generally indicative of the manner in which a multilayer film structure is built up. That is, in general, the first layer can be present without any of the additional layers described, or the first and second layers can be present without any of the additional layers described, etc.

As used herein, the term "extrusion" is used with reference to the process of forming continuous shapes by forcing a molten plastic material through a die, followed by cooling or chemical hardening. Immediately prior to extrusion through the die, the relatively high-viscosity polymeric material is fed into a rotating screw of variable pitch, i.e., an extruder, which forces the polymeric material through the die.

As used herein, the term "coextrusion" refers to the process by which the outputs of two or more extruders are brought smoothly together in a feed block, to form a multilayer stream that is fed to a die to produce a layered extrudate. Coextrusion can be employed in film blowing, sheet and flat film extrusion, blow molding, and extrusion coating.

As used herein, the phrase "machine direction", herein abbreviated "MD", refers to a direction "along the length" of the film, i.e., in the direction of the film as the film is formed during extrusion and/or coating. As used herein, the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine or longitudinal direction.

As used herein, the phrase "free shrink" refers to the percent dimensional change in a 10 cm x 10 cm specimen of film, when shrunk at 185°F, with the quantitative determination being carried out according to ASTM D 2732, as set forth in the <u>1990 Annual Book of ASTM Standards</u>, Vol. 08.02, pp. 368-371, which is hereby incorporated, in its entirety, by reference thereto.

Although the film useful in the article of the present invention has at least 1 layer (more preferably, from 1 to 20 layers), more preferably the film has from 1 to 12 layers, still more preferably, from 1-8 layers; and, yet still more preferably, from 1-4 layers. However, so long as the multilayer film has at least 3 layers, the multilayer film can have any further number of additional layers desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used, e.g., O_2-barrier characteristics, free shrink, shrink tension, optics, modulus, seal strength, etc. The multilayer film illustrated in Figure 2 has four layers. However, since the middle layer is preferably formed from the

collapsing of a two-layer tubing film upon itself, the middle layer is actually two distinct layers itself, so that the film, in reality, contains four layers.

The film used in the present invention has a thickness of at least 1.5 mils (1 mil equals 0.001 inch); preferably, a thickness of from about 1.5 to 20 mils; more preferably, from about 2 to 20 mils; still more preferably, from about 2 to 7 mils; and yet still more preferably, from about 3 to 5 mils. Of course, the preferred thickness varies depending upon the desired properties for the particular packaging operation in which the film is used.

Figure 1 is a side-view illustration of a preferred article (an end-seal bag) in accordance with the present invention. In Figure 1, end-seal bag 10 is illustrated in lay-flat position. End-seal bag 10 is made from film 12, with end-seal bag 10 having open top 14 and end-seal 16.

Figure 2 is a side-view illustration of another preferred article (a side-seal bag) in accordance with the present invention. In Figure 2, side-seal bag 20 is illustrated in lay-flat position. Side-seal bag 20 is also made from film 12, and side seal bag has open top 22, and side seals 24 and 26.

Figure 3 is a side-view illustration of another preferred article (a pouch) in accordance with the present invention. In Figure 3, pouch 30 is illustrated in lay-flat position. Pouch 30 is also made from film 12, has open top 32, and side seals 34 and 36 and end seal 38.

Figure 4 illustrates a cross-sectional view of preferred 4-layer film 12 in accordance with the present invention. In Figure 4, Film 12 has first layer 42, which is a first outer film layer, inner film layers 44 and 46, and second outer film layer 48. Preferably, first outer layer 42 comprises EVA and LLDPE, and is free of carbon-black. Preferably, second outer layer 48 comprises HDPE, and is also free of carbon black. Preferably, inner film layer 44 comprises EVA, LLDPE, and carbon black. Preferably, inner layer 46 comprises EVA.

Figure 5 illustrates a cross-sectional view of preferred 9-layer film 50 in accordance with the present invention. In Figure 5, Film 50 has: (1) first layer 52, which is an outer layer which preferably comprises EVA and LLDPE, but is free of carbon black; (2) second layer 54 which is an inner layer between the first layer and the third layer, and which preferably comprises EVA and LLDPE, and which also comprises carbon black; (3) third layer 56 which is also an inner layer between the second layer and the seventh layer, and which

preferably comprises EVA, but is free of carbon black; (4) fourth layer 58 which is an outer layer which preferably comprises HDPE, and which is free of carbon black; (5) fifth layer 60 which is an inner layer between the sixth layer and the eighth layer, and which preferably comprises EVA and LLDPE, but is free of carbon black; (6) sixth layer 62 which is an inner layer between the seventh layer and the fifth layer, and which preferably comprises EVA and LLDPE, and which also comprises carbon black; (7) seventh layer 63 which is an inner layer between the third layer and the sixth layer, and which preferably comprises EVA, but is free of carbon black; (8) eighth layer 64 which is an inner layer between the fifth layer and the ninth layer, and which preferably comprises polyvinylidene chloride, and which is free of carbon black; and (9) ninth layer 65 which is an inner layer between the eighth layer and the fourth layer, and which preferably comprises biaxially oriented polypropylene, and which is free of carbon black.

Figure 6 illustrates a schematic of a preferred process for producing a substrate film which makes up the first, second, and third layers of the multilayer films of Figure 4, and the first, second, third, fifth, sixth, and seventh layers of the multilayer film of Figure 5. In the process illustrated in Figure 6, solid polymer beads (not illustrated) are fed to a plurality of extruders 66 (for simplicity, only one extruder is illustrated). Inside extruders 66, the polymer beads are forwarded, melted, and degassed, following which the resulting bubble-free melt is forwarded into die head 68, and extruded through annular die, resulting in tubing 70, which is 5-40 mils thick, more preferably 20-30 mils thick, still more preferably, about 25 mils thick.

After cooling or quenching by water spray from cooling ring 72, tubing 70 is collapsed by pinch rolls 74, and is thereafter fed through irradiation vault 76 surrounded by shielding 78, where tubing 70 is irradiated with high energy electrons (i.e., ionizing radiation) from iron core transformer accelerator 80. Tubing 70 is guided through irradiation vault 76 on rolls 82. Preferably, the irradiation of tubing 70 is at a level of from about 2 to 10 megarads (hereinafter "MR"); more preferably, from about 3.5-4 MR.

After irradiation, irradiated tubing 84 is directed over guide roll 86, after which irradiated tubing 84 passes into hot water bath tank 88 containing water 90. The now-collapsed irradiated tubing 84 is submersed in the hot water for a retention time of at least about 5 seconds, i.e., for a time period in order to bring the film up to the desired

temperature, following which supplemental heating means (not illustrated) including a plurality of steam rolls around which irradiated tubing 84 is partially wound, and optional hot air blowers, elevate the temperature of irradiated tubing 84 to a desired orientation temperature of from about 240°F-250°F. Thereafter, irradiated film 84 is directed through nip rolls 92, and bubble 94 is blown, thereby transversely stretching irradiated tubing 84 to form oriented blown tubing film 96. Furthermore, while being blown, i.e., transversely stretched, irradiated tubing 84 is drawn (i.e., in the longitudinal direction) between nip rolls 88 and nip rolls 98, as nip rolls 98 have a higher surface speed than the surface speed of nip rolls 92. As a result of the transverse stretching and longitudinal drawing, irradiated, biaxially-oriented, blown tubing film 96 is produced, this blown tubing preferably having been both stretched at a ratio of from about 1:1.5 - 1:6, and drawn at a ratio of from about 1:1.5-1:6. More preferably, the stretching and drawing are each performed at a ratio of from about 1:2 - 1:4. The result is a biaxial orientation of from about 1:2.25 - 1:36, more preferably, 1:4 - 1:16. While bubble 94 is maintained between pinch rolls 92 and 98, blown tubing film 96 is collapsed by converging rolls 100, and thereafter conveyed through pinch rolls 98 and across guide roll 102, and then rolled onto wind-up roller 104. Idler roll 106 assures a good wind-up.

Preferably, one or more additional films are preferably laminated to the substrate film preferably produced as described immediately above. For example, in one preferred embodiment of the present invention, a four-layer substrate film is laminated to a monolayer film of HDPE. In another, a six-layer substrate film is first laminated to a multilayer film having a first layer of PVDC and a second layer of biaxially oriented polypropylene, with the resulting laminate then being further laminated to a monolayer film comprising high density polyethylene, to result in the film of Figure 5.

The film of the present invention is preferably irradiated to induce crosslinking, as well as corona treated to roughen the surface of the films which are to be adhered to one another. In the irradiation process, the film is subjected to an energetic radiation treatment, such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray, and high energy electron treatment, which induce cross-linking between molecules of the irradiated material. The irradiation of polymeric films is disclosed in U.S. Patent NO. 4,064,296, to BORNSTEIN, et. al., which is hereby incorporated in its entirety, by reference thereto.

BORNSTEIN, et. al. discloses the use of ionizing radiation for crosslinking the polymer present in the film.

The corona treatment of a film is performed by subjecting the surfaces of the film to corona discharge, i.e., the ionization of a gas such as air in close proximity to a film surface, the ionization initiated by a high voltage passed through a nearby electrode, and causing oxidation and other changes to the film surface, such as surface roughness. Corona treatment of polymeric materials is disclosed in U.S. Patent No. 4,120,716, to BONET, issued October 17, 1978, herein incorporated in its entirety by reference thereto, discloses improved adherence characteristics of the surface of polyethylene by corona treatment, to oxidize the polyethylene surface. U.S. Patent No. 4,879,430, to HOFFMAN, also hereby incorporated in its entirety by reference thereto, discloses the use of corona discharge for the treatment of plastic webs for use in meat cook-in packaging, with the corona treatment of the inside surface of the web to increase the adhesion of the meat to the adhesion of the meat to the proteinaceous material.

In general, sealing of film to produce a bag can be performed using a hot bar (heat seal) or a nichrome wire fixed to a chilled metal bar (impulse seal), as is known to those of skill in the art, or any other sealing means known to those of skill in the art, such as ultrasonic radiation, radio frequency radiation, and laser. The preferred sealing means is an impulse sealer. Films which are predominantly polyethylene are generally sealed using impulse sealing or hot bar sealing. Both linear and shaped seals can be formed, as is known to those of skill in the art. In general, sealing and cutting of tubing to produce bags is disclosed in U.S. Patent No. 3,552,090, U.S. Patent No. 3,383,746, and U.S. Serial No. 844,883, filed July 25, 1969, to OWEN, each of these two U.S. Patents as well as the U.S. Patent application, hereby being incorporated by reference thereto, in their entireties.

Various films suitable for use in the article of the present invention are illustrated by the following examples. Unless stated otherwise, all percentages, parts, etc. are by weight.

Examples

A coextruded, three-ply tubular tape was cast, the tape having a thickness of 29 mils, the tape having an A (outside)layer making up 25 percent of the tape thickness, and a B (inner) layer making up 60 percent of the tape thickness, and a C (inside) layer making up 15% of the tape thickness. The A layer was composed of: (a) 90 weight percent DOWLEX

2045 (TM) linear low density polyethylene having a density of 0.920 g/cc, obtained from The Dow Chemical Company, of Midland, Michigan (hereinafter "LLDPE #1"), (b) 10 weight percent ESCORENE® LD 318.92 ethylene/vinyl acetate copolymer having a vinyl acetate content of 9 percent, obtained from the Exxon Chemical Company of Houston, Texas "EVA #1." The B layer was composed of: (a) 65 weight percent LLDPE #1; (b) 10 weight percent EVA #1; and (c) 25 weight percent 19153-S black low density polyethylene-based masterbatch, obtained from Ampacet Corporation, of Terrytown, New York, hereinafter "Black Masterbatch #1." The C layer was composed of 100 percent ESCORENE® LD-761.36 ethylene/vinyl acetate copolymer having a vinyl acetate content of 28 percent, obtained from the Exxon Chemical Company, of Houston, Texas, hereinafter "EVA #2."

The three-ply tubing was cooled to a solid phase in a water bath and then electronically crosslinked to a level of from about 53.2 milliamps (i.e., 7 to 8 megarads "MR"). The resulting crosslinked three-ply tubing was heated by steam cans and hot air at about 237°F, and was subsequently oriented by being drawn and stretched approximately 350%, in each of the machine and transverse directions, respectively, using a trapped bubble of air held between two nip rolls. The orientation produced a 2.38 mil three-ply film in the form of a tube.

After drawing, the resulting coextruded, hot-water-shrinkable lay-flat film tubing was passed through a pair of nip rolls, causing the inside C layer to bond to itself upon tube collapse, rendering a final six-ply film, with the two central plies being the inside C layer bonded to itself (i.e., resulting in a "self-welded 6-ply film" having a thickness of 4.76 mils), as follows:

A / B / C / C / B / A

Side-seal bags were formed from the self-welded 6-ply film, by sealing the film to itself using a VERTROD® impulse sealer (model 84 EPCS) which utilized a ribbon-type seal element having a width of about 0.25 inch, with the upper jaw being applied to force the (folded-over) film against itself and seal element while the seal jaw was heated up to a 300°F while in contact with the film, and thereafter allowed to cool to temperature of about 200°F (with a dwell time on the film of about 10 seconds), and a pressure of about 60 psi. The resulting side-seal bags had a width of about 9 inches and a length of about 15 inches long.

The resulting side-seal bags were placed between parallel walls about 2-3 inches apart, i.e., a "parallel plate burst test", with the bags thereafter being inflated until the bag burst. The failure always occurred in the region adjacent the seal. The seal did not fail. The amount of pressure inside the bag at the point of failure was a measure of parallel plate burst strength. Five bags made from the self-welded 6-ply film had mean burst strengths of 269, 240, 269, 268, and 275 inches of water.

In a second variation, the six-ply self-welded film can be laminated to two additional films, i.e., a second film and a third film. The second film has two layers (i.e., layers D and E) and a total thickness of 1.0 mil. The lamination of the 6-layer film is to a first layer of the second film, this first layer having a thickness of about 0.8 mil and comprising 100% biaxially oriented polypropylene. The second layer of the second film has a thickness of about 0.2 mils and comprises 100% polyvinylidene chloride. To the resulting laminate is further laminated a third film which was a monolayer film having a thickness of about 1 mils, with 100 weight percent of the third film being ALATHON® M6210 high density polyethylene (HDPE) having a density of 0.960 g/cc, obtained from Lyondell Polymers, of Houston, Texas. In the resulting 9-layer laminate structure (plus two additional layers which contain adhesives used in lamination), the first layer of the second film serves as a moisture barrier layer, while the second layer of the second film serves as both a moisture-barrier and O_2-barrier layer. The sole layer of the third film serves as a moisture barrier layer in the resulting laminate. The adhesive used to laminate the films together is preferably a urethane-based adhesive, such as LIOFOL® 7975 urethane-based adhesive.

A second variation of the above film can be made by producing a hot blown five-layer film having an A/B/C/B/A structure in which A is 100% HDPE, B is anhydride-modified high density polyethylene, and C is ethylene/vinyl alcohol copolymer (EVOH). A preferred layer thickness ratio for the A/B/C/B/A film is 5/1/1/1/5. This five-layer film is then laminated to the self-welded six-layer film described above.

In yet a third variation, the EVOH in the second variation structure described immediately above is replaced by acrylonitrile methacrylate copolymer, e.g., BAREX® acrylonitrile methacrylate copolymer, obtained from BP Chemical Corporation of Warrenville Heights, Ohio.

In a fourth variation, the EVOH in the second variation structure described above is replaced with 100% amorphous nylon, e.g., SELAR PA® amorphous nylon, or a blend of 1-90 weight percent EVOH and 99 to 10 weight percent amorphous nylon, e.g., SELAR PA® amorphous nylon.

Any of the four laminate variations described above can be further coated so that a peelable seal or other easy-open package can be formed, e.g.: as disclosed in U.S. Patent No. 4,680,340, to Oreglia et al; U.S. Patent No. 4,859,514, to Friedrich et al; U.S. Patent No. 5,023,121, to Pockat et al, each of which is hereby incorporated in its entirety, by reference thereto. Such easy open packages are especially useful for the packaging of motion picture film rolls.

In the packaging of photography-related products, the film and article of the present invention are especially useful for the packaging of 10 to 100 pound rolls of photographic paper and photographic film, as well as for the packaging of various sizes of motion picture film rolls. The layer(s) of embedded carbon black, which are blended with polymer, to prevent a light-sensitive product in the package from being exposed to light.

Although the present invention has been described in connection with the preferred embodiments, it is to be understood that modifications and variations may be utilized without departing from the principles and scope of the invention, as those skilled in the art will readily understand. Accordingly, such modifications may be practiced within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A multilayer film comprising:

(A) a first layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(B) a second layer comprising carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(C) a third layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(D) a fourth layer comprising at least one member selected from the group consisting of high density polyethylene, propylene homopolymer, polyvinylidene chloride, fluoropolymer, and aluminum;

wherein the second layer is between the first layer and the third layer, and the third layer is between the second layer and the fourth layer.

2. The multilayer film according to Claim 1, wherein the fourth layer has a moisture vapor transmission rate of less than about 0.3 grams/100sq.in. at 100°F and 90% relative humidity.

3. The multilayer film according to Claim 1, wherein the multilayer film has a thickness of from about 2 to 10 mils.

4. The article according to Claim 1, wherein at least a portion of the film has been irradiated to a level of from about 50 to 150 kilograys.

5. The multilayer film according to Claim 1, wherein the film has a total free shrink, at 185°F, of less than about 30 percent.

6. The multilayer film according to Claim 1, wherein the fourth layer comprises high density polyethylene, and wherein the multilayer film further comprises:

(A) a fifth layer comprising at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, polyvinylidene chloride, polyamide, polyester, aluminum, and polyacrylonitrile, the fifth layer being between the third layer and the fourth layer; and

(B) a sixth layer comprising biaxially oriented polypropylene, the sixth layer being between the third layer and the fourth layer.

7. The multilayer film according to Claim 1, further comprising:

(A) a fifth layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester, the fifth layer being between the third layer and the fourth layer;

(B) a sixth layer comprising carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester, the sixth layer being between the third layer and the fifth layer; and

(C) a seventh layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester, the seventh layer being between the third layer and the sixth layer.

8. The multilayer film according to Claim 7, wherein the first, second, third, fifth, sixth, and seventh layers comprise a structure which is symmetrical in both thickness and chemical composition.

9. The multilayer film according to Claim 7, further comprising an eighth layer comprising:

(A) from about 1 to 40 weight percent of a first polymer comprising at least one member selected from the group consisting of ionomer and ethylene/vinyl acetate copolymer, wherein the first polymer has a melt flow index of less than 5 grams/10 minutes; and

(B) from about 60 to 99 weight percent of a second polymer comprising at least one member selected from the group consisting of low density polyethylene, ethylene/vinyl acetate copolymer, and modified ethylene/vinyl acetate copolymer, the second polymer having a melt index greater than 20 g/10 min, wherein the second polymer comprises low density polyethylene if the first polymer comprises ethylene/vinyl acetate copolymer.

10. The multilayer film according to Claim 7, wherein a copolyester is present in at least one member selected from the group consisting of the first layer, the second layer, the third layer, the fifth layer, the sixth layer, and the seventh layer.

11. The multilayer film according to Claim 7, wherein:

the first, second, fifth, and sixth layers each comprise a blend of ethylene/vinyl acetate copolymer and linear low density polyethylene;

the third and seventh layers each comprise ethylene/vinyl acetate copolymer; and

the fourth layer comprises high density polyethylene.

12. The multilayer film according to Claim 7, wherein the film first, second, third, fifth, sixth, and seventh layers each comprise biaxially oriented polymer.

13. The multilayer film according to Claim 7, wherein at least the first, second, third, fifth, sixth, and seventh layers comprise a crosslinked polymer network.

14. The multilayer film according to Claim 7, wherein the multilayer film has an O_2-transmission rate of less than about 100 cc/m^2 day stp at 100% relative humidity.

15. The multilayer film according to Claim 7, wherein the fourth layer comprises high density polyethylene, and wherein the multilayer film further comprises:

(A) an eighth layer comprising high density polyethylene, the eighth layer being between the fifth layer and the fourth layer; and

(B) a ninth layer comprising at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, polyvinylidene chloride, amorphous polyamide, polyester, and polyacrylonitrile, the eighth layer being between the fifth layer and the fourth layer.

16. The multilayer film according to Claim 7, wherein the fourth layer comprises high density polyethylene, and wherein the multilayer film further comprises:

(A) an eighth layer comprising at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, polyvinylidene chloride, amorphous polyamide, polyester, and polyacrylonitrile, the eighth layer being between the fifth layer and the fourth layer; and

(B) a ninth layer comprising biaxially oriented polypropylene, the ninth layer being between the fifth layer and the fourth layer.

17. The multilayer film according to Claim 16, wherein the ninth layer comprises biaxially-oriented polypropylene.

18. The multilayer film according to Claim 17, wherein the ninth layer comprises propylene homopolymer in an amount of from about 60 to 99 weight percent, based on layer weight, and hydrocarbon resin in an amount of from about 1 to 40 weight percent, based on layer weight.

19. The multilayer film according to Claim 16, wherein a copolyester is present in at least one member selected from the group consisting of the first layer, the second layer, the third layer, the fifth layer, the sixth layer, the seventh layer, and the eighth layer.

20. The multilayer film according to Claim 16, wherein:

the first, second, fifth, and sixth layers each comprise a blend of ethylene/vinyl acetate copolymer and linear low density polyethylene;

the third and seventh layers each comprise ethylene/vinyl acetate copolymer;

the fourth layer comprises high density polyethylene;

the eighth layer comprises polyvinylidene chloride; and

the ninth layer comprises biaxially oriented polypropylene.

21. An easy-open article having a peel opening force of less than about 2.5 pounds per inch, the article comprising a first film sealed to itself or a second film, wherein the first film comprises:

(A) an first layer which is an outer film layer and which serves as a seal layer, the first layer comprising:

(i) from about 1 to 40 weight percent of a first polymer comprising at least one member selected from the group consisting of ionomer and ethylene/vinyl acetate copolymer, wherein the first polymer has a melt flow index of less than 5 g/10 min; and

(ii) from about 60 to 99 weight percent of a second polymer comprising at least one member selected from the group consisting of low density polyethylene, ethylene/vinyl acetate copolymer, and modified ethylene/vinyl acetate copolymer, the second polymer having a melt index greater than 20 g/10 min, wherein the second polymer comprises low density polyethylene if the first polymer comprises ethylene/vinyl acetate copolymer; and

(B) a second layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene,

ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(C) a third layer comprising carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(D) a fourth layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(E) a fifth layer comprising at least one member selected from the group consisting of high density polyethylene, propylene homopolymer, polyvinylidene chloride, fluoropolymer, and aluminum;

wherein the third layer is between the second layer and the fourth layer, and the fourth layer is between the third layer and the fifth layer.

22. An article comprising a multilayer film sealed to itself or another film, wherein the multilayer film comprises:

(A) a first layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(B) a second layer comprising carbon black pigment and at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate copolymer, ethylene/butyl acetate copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(C) a third layer comprising at least one member selected from the group consisting of linear low density polyethylene, very low density polyethylene, ethylene/vinyl acetate

copolymer, ethylene/butyl acetate copolymer, ionomer, homogeneous ethylene/alpha-olefin copolymer, polyamide, and polyester;

(D) a fourth layer comprising at least one member selected from the group consisting of high density polyethylene, propylene homopolymer, polyvinylidene chloride, fluoropolymer, and aluminum;

wherein the second layer is between the first layer and the third layer, and the third layer is between the second layer and the fourth layer.

23. The article according to Claim 22, wherein the article is an end-seal bag, side-seal bag, L-seal bag, pouch, and backseamed casing.

24. The article according to Claim 22, wherein the article has a burst strength of at least about 200 inches of water.

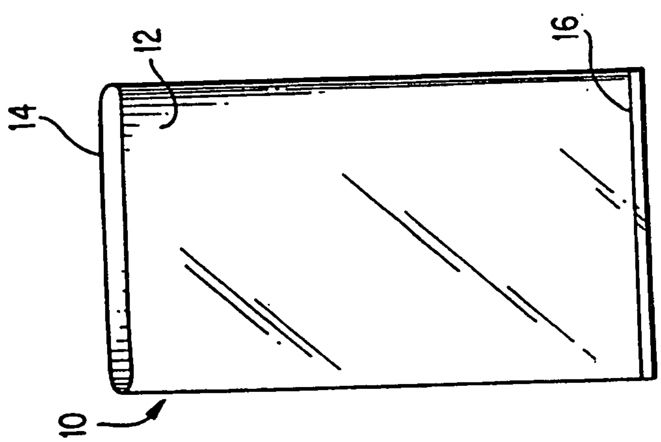

FIG. 1

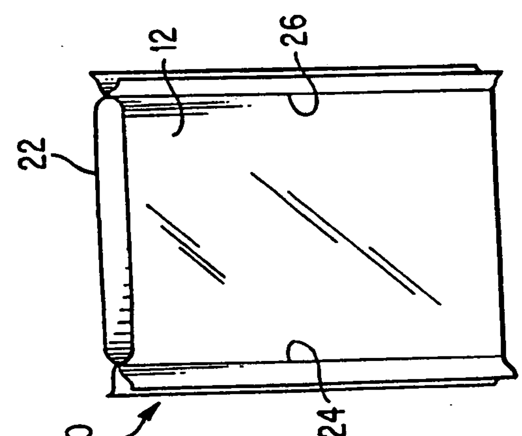

FIG. 2

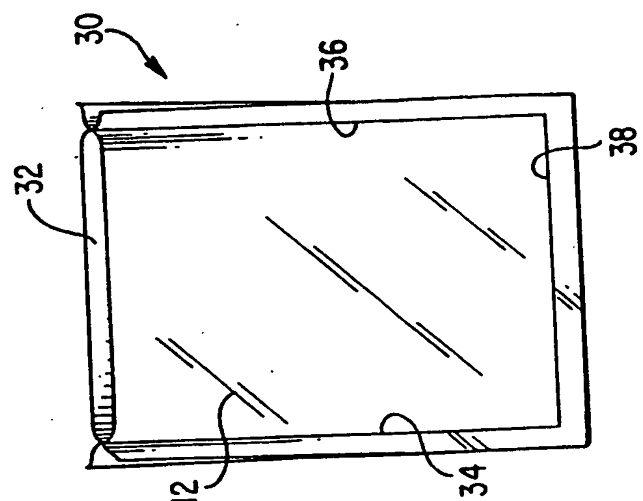

FIG. 3

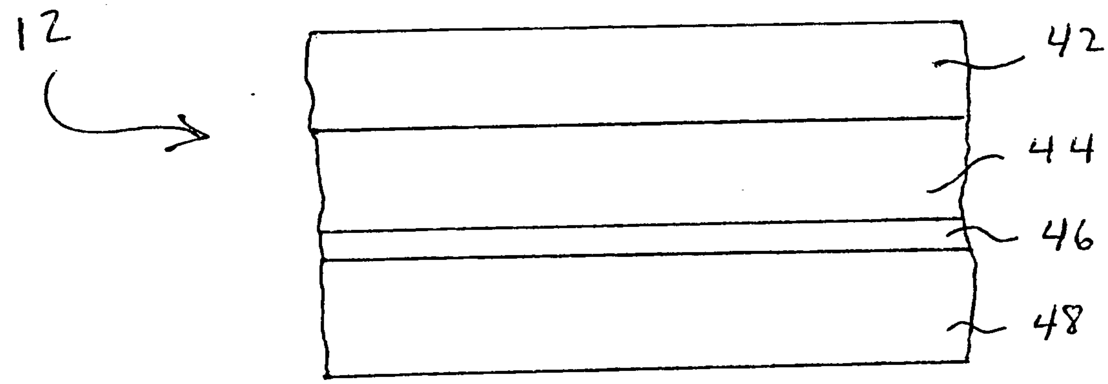

FIG. 4

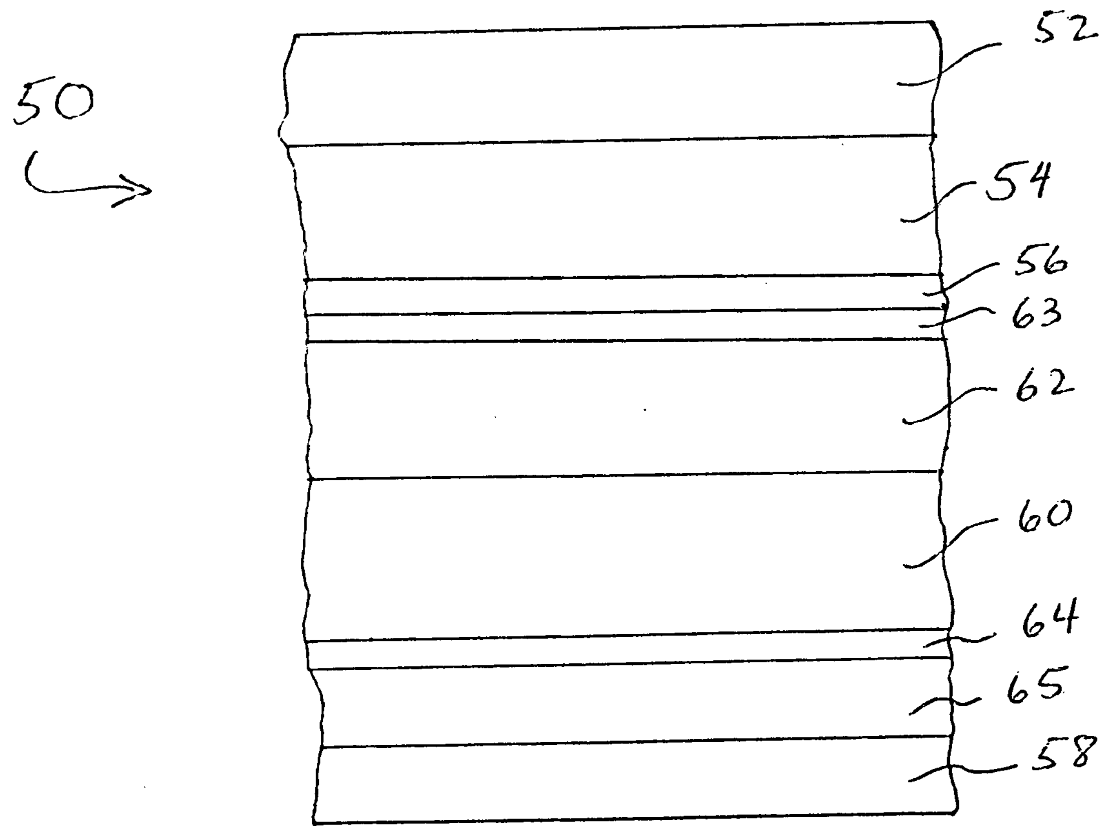

FIG. 5

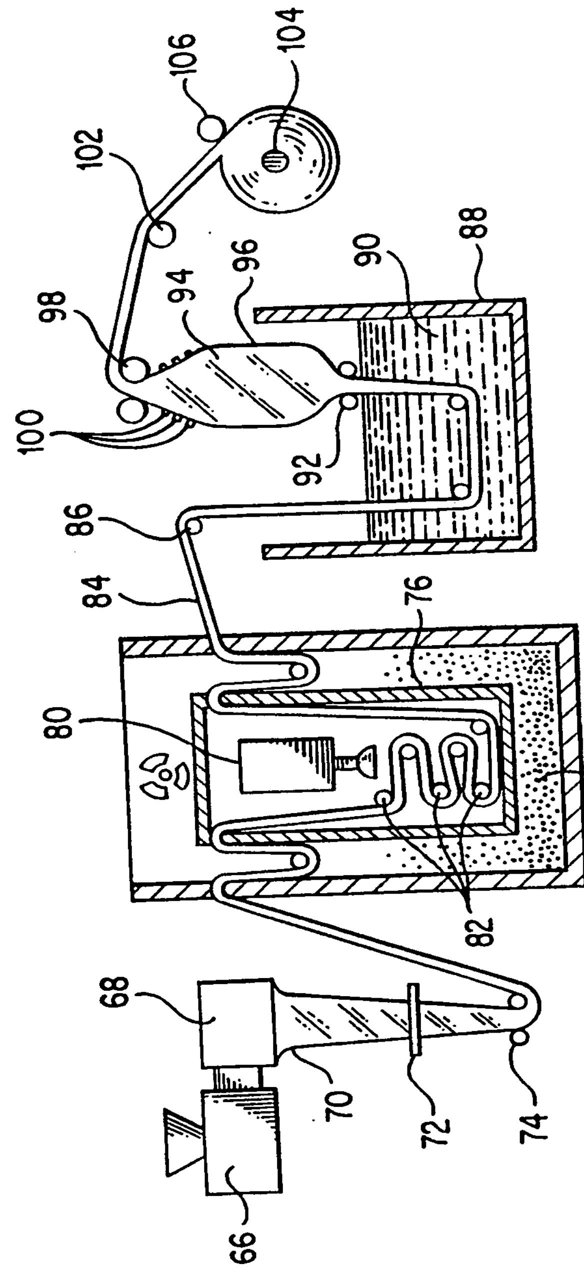

FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/03036

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/08 B32B27/20 B65D65/40 G03C3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 082 744 A (AKAO MUTSUO ET AL) 21 January 1992 see claim 1 see column 5, line 18 - line 36; examples 19,20; table 4	1-3,22
X	US 5 118 563 A (AKAO MUTSUO) 2 June 1992 see claim 1 see column 4, line 60 - line 69 see column 10, line 5 - line 38; figure 2; table 1	1-3,22
A		6
X	US 5 227 255 A (AKAO MUTSUO) 13 July 1993 see claim 1 see figure 3; example III: table 1	1-3,22
A		6

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 June 1998	29/06/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ibarrola Torres, O

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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